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(54) **Base beads for manufacture of detergent compositions**

(57) Free-flowing base beads, into which nonionic detergent in liquid form may be absorbed to make a free-flowing particulate built synthetic nonionic organic detergent product of improved washing properties, include 15 to 30% of sodium carbonate, 10 to 22% of sodium bicarbonate, 10 to

50% of water softening aluminium silicate (zeolite), 0 to 18% of sodium silicate, 1 to 20% of bentonite and/or 0.05 to 2% of polyacrylate of molecular weight in the range of 1,000 to 5,000, and 1 to 15% of moisture, together with suitable adjuvants and processing aids in small proportions (normally totalling less than 10% and preferably less than 5%).

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SPECIFICATION

Base beads for manufacture of detergent compositions

5 This invention relates to base beads which are
useful for the manufacture of built nonionic
detergent compositions. More particularly, it
relates to such beads which are essentially
inorganic in nature and include sodium carbonate,
sodium bicarbonate, zeolite, sodium silicate and
bentonite and/or polyacrylate and which can
absorb nonionic detergent, in liquid form, to make
freely flowing, particulate, built nonionic
detergent compositions. The invention also
relates to manufacturing processes, crutcher
slurries and detergent compositions made
therefrom, which compositions are of improved
washing properties, depositing less residue on
washed materials despite the presences of zeolite
and silicate.

20 Synthetic organic detergent compositions
containing water softening aluminium silicates,
such as zeolites, have been marketed in recent
years. In such compositions, which also include a
synthetic organic detergent or surface active
agent component, the zeolite acts as a calcium
sequestrant and as a builder for the organic
detergent, improving its cleaning effects,
especially in hard water. In such compositions
sodium silicate has also been employed as a
builder and as a corrosion preventing additive, to
protect aluminium parts of washing equipment
with which aqueous solutions of the detergent
compositions come in contact during washing
operations. The silicate also may be useful in
counteracting adverse effects magnesium ions in
the wash water could have on the washing
activity of the detergent composition.
Additionally, it is considered that the silicate helps
to produce more stable detergent beads,
especially when such are made by spray drying of
a crutcher mix of detergent composition
components. However it is well recognized that
zeolites often tend to deposit as a noticeable
residue on laundry washed in aqueous cleaning
media containing them, and various investigators
have reported that the presence of a silicate in
such a medium with zeolite increases the amount
of residue deposited.

50 Bentonite, a swelling clay, with comparatively
minor hardness ion exchange capacity, has been
suggested for use in various detergent products,
such as soap bars and laundry detergents,
wherein it has often served primarily as a filler.
However, in some instances it is alleged to
perform other functions. For example, in U.S.
patent 4,166,039 it is taught to aid in the
production of homogeneous detergent slurries
when such slurries contain phosphate(s).
Normally however, the incorporation of clays in
detergent compositions is avoided because they
are insoluble and might be expected to deposit on
the materials being laundered. In fact, clay soil
removal is one of the tests utilized to rate
detergent effectiveness. Despite the fact that it

65 might be expected that the addition of bentonite
would only exacerbate residue problems
encountered when washing laundry with aqueous
media containing detergent compositions
incorporating zeolite and silicate, surprisingly it
has been found that residue deposition is
diminished. Also, calcium ion binding rates are
increased.

70 Polyacrylates, often of comparatively high
molecular weight, have been suggested as
detergent composition components. They have
been disclosed to be components of powdered and
slurried detergents and have been suggested as
replacements for phosphate builders in non-
phosphate detergents. It is known that the
polyacrylates possess dispersing properties and a
manufacturer of these materials has suggested
them for use in dispersing applications, as in
maintaining the suspension of pigments in paints.
Additionally, it is known that in certain aqueous
media they tend to inhibit deposition of insoluble
calcium compounds and redeposition of insoluble
materials on washed laundry. Although
polyacrylates have been included in detergent
formulations, the present crutcher mixes, base
beads and detergent compositions are considered
to be novel and unobvious. The presence of the
very small quantity of a particular type of
polyacrylate in the specified formulations, in co-
operation with the other components of such
formulations, has been found to result in an
improved product of better cleaning
characteristics, which can be made using
practicable manufacturing operations.

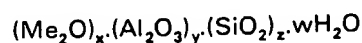
100 In accordance with the present invention free
flowing base beads, on which nonionic detergent
may be absorbed to make particulate built
synthetic nonionic organic detergent products of
improved washing properties, which, after rinsing
leave lesser amount of deposits on fabrics
washed with such products, comprise by weight
from about 15 to 30% of sodium carbonate, 10 to
22% of sodium bicarbonate, 10 to 50% of water
softening aluminium silicate, 0 to 18% of sodium
silicate, and 1 to 20% of bentonite and/or 0.05 to
2% of polyacrylate of molecular weights in the
range of 1,000 to 5,000. Such products will
normally contain from 1 to 15% of moisture and
may be made into organic detergent
compositions by application of liquid state
nonionic detergent to them so that the detergent
is absorbed and the product resulting is still free
flowing. The proportion of detergent utilized will
normally be such that the final detergent
composition will contain about 8 to 30% thereof,
by weight. The presence of the polyacrylate helps
to make the base beads more absorptive of the
liquid nonionic detergent. Also, it often improves
spray drying operations, resulting in less material
adhering to the dryer walls and thereby increasing
spray tower throughput rates and diminishing the
number of cleanouts which may be required.

125 The various components of the base beads of
this invention, except for water, are normally in
the solid state, although, when added to the

crutcher, some may be in the forms of hydrates or may be dissolved or dispersed in an aqueous medium, such as water. The sodium bicarbonate is preferably anhydrous and sodium carbonate is generally utilized as soda ash. Yet, the carbonate hydrates, such as the monohydrate, may be employed, if desired, and in some cases it may be possible to utilize other carbonates and bicarbonates, such as other alkali metal salts, e.g., the potassium salts, in replacement of at least some of the sodium salt, although the sodium salts are highly preferred. The silicate, when present, is usually added to the crutcher as an aqueous solution, which is normally of 40 to 50% solids content, e.g., 47.5%, and preferably its addition is near the end of the mixing process. The silicate employed will usually be of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio within the range of 1:1.4 to 1:3, preferably 1:1.6 to 1:2.4 or 1:2.6 and more preferably 1:2 to 1:2.4. Although sodium silicate is the preferred silicate, a portion of the sodium silicate may be replaced by potassium silicate or other suitable soluble alkali metal silicate salt.

The zeolites employed include crystallines, amorphous and mixed crystalline-amorphous zeolites of both natural and synthetic origins which are satisfactorily quick and sufficiently effective activities in counteracting calcium hardness ions in wash waters. Preferably, such materials are capable of reacting sufficiently rapidly with the calcium ions so that, alone or in conjunction with other water softening compounds in the detergent, they soften the wash water before adverse reactions of such ions with other components of the synthetic organic detergent composition occur. The zeolites employed may be characterised as having a high exchange capacity for calcium ion, which is normally from about 200 to 400 or more milligram equivalents of calcium carbonate hardness per gram of the aluminosilicate, preferably 250 to 350 mg. eq/g. Also they preferably have a hardness depletion rate residual hardness of 0.02 to 0.05 mg. CaCO_3 /litre in one minute, preferably 0.02 to 0.03 mg./l., and less than 0.01 mg./l. in 10 minutes, all on an anhydrous zeolite basis.

Although other ion exchanging zeolites may also be utilized, normally the finely divided synthetic zeolite builder particles employed in the practice of this invention will be of the formula



wherein Me represents a metal of other suitable cationic material, x is 1, y is from 0.8 to 1.2, preferably about 1, z is from 1.5 to 3.5, preferably 2 to 3 or about 2 and w is from 0 to 9, preferably 2.5 to 6.

The zeolite should preferably be a univalent cation-exchanging zeolite, i.e., it should be an aluminosilicate of a univalent cation such as sodium, potassium, lithium (when practicable) or other alkali metal, ammonium or hydrogen

(sometimes). Preferably the univalent cation of the zeolite that is employed is an alkali metal cation, especially sodium or potassium, and most preferably is sodium.

Crystalline types of zeolites utilizable as good ion exchangers in the invention, at least in part, include zeolites of the following crystal structure groups; A, X, Y, L mordenite and erionite, of which types A, X, and Y are preferred. Mixtures of such molecular sieve zeolites can also be useful, especially when type A zeolite is present. These crystalline types of zeolites are well known in the art and more particularly described in the text *Zeolite Molecular Sieves* by Donal W. Breck, published in 1974 by John Wiley & Sons. Typical commercially available zeolites of the aforementioned structural types are listed in Table 9.6 at pages 747—749 of the Breck text. Such zeolites are known in the art. Some, and other such suitable zeolites have been described in many patents in recent years for use as detergent composition builders.

The zeolite used in the invention is usually synthetic and it is often characterized by having a network of substantially uniformly sized pores in the range of about 3 to 10 Angstroms, often being about 4 Å (nominal), such size being uniquely determined by the unit structure of the zeolite crystal. Preferably it is of the type A or similar structure, particularly described at page 133 of the aforementioned text. Good results have been obtained when a type 4A molecular sieve zeolite is employed, wherein the univalent cation of the zeolite is sodium and the pore size of the zeolite is about 4 Angstroms. Such zeolite molecular sieves are described in U.S. patent 2,882,243, which refer to them as Zeolite A.

Molecular sieve zeolites can be prepared in either a dehydrated or calcined form which contains from about 0 or about 1.5% to about 3% of moisture or in a hydrated or water loaded form which contains additional bound water in an amount from about 4% up to about 36% of the zeolite total weight, depending on the type of zeolite used. The water containing hydrated form of the molecular sieve zeolite (preferably about 15 to 70% hydrated) is preferred in the practice of this invention when such crystalline product is used. The manufacture of such crystals is well known in the art. For example, in the preparation of Zeolite A, referred to above, the hydrated zeolite crystals that are formed in the crystallization medium (such as a hydrous amorphous sodium aluminosilicate gel) are used without the high temperature dehydration (calcining to 3% or less water content) that is normally practiced in preparing such crystals for use as catalysts, e.g., cracking catalysts. The crystalline zeolite, in either completely hydrated or partially hydrated form, can be recovered by filtering off the crystals from the crystallization medium and drying them in air at ambient temperature so that their water contents are in the range of about 5 to 30% moisture, preferably about 10 to 25%, such as 17 to 22%. However,

the moisture content of the molecular sieve zeolite being employed may be much lower, as was previously described, in which case the zeolite will usually be hydrated during crutching and other processing.

5 Preferably the zeolite should be in a finely divided state with the ultimate particle diameters being up to 20 microns, e.g., 0.005 or 0.01 to 20
10 microns, preferably being from 0.01 to 15 microns and especially preferably of 0.01 to 8 microns mean particle size, e.g., 3 to 7 or 12 microns, if crystalline, and 0.01 to 0.1 micron, e.g., 0.01 to 0.05 micron, if amorphous. Although
15 the ultimate particle sizes are much lower, usually the zeolite particles will be of sizes within the range of 100 to 400 mesh, preferably 140 to 325 mesh. These are U.S. mesh sizes; U.S. 100 mesh has openings of 149 microns, 140 mesh of 105 microns, 325 mesh of 44 microns and 400 mesh
20 of 37 microns.

Zeolites of smaller sizes will often become objectionably dusty and those of larger sizes may not sufficiently and satisfactorily cover the carbonate-bicarbonate base particle nuclei on
25 which they may be deposited.

The bentonite employed is preferably a colloidal clay (aluminium silicate) containing montmorillonite. Montmorillonite is a hydrated aluminium silicate in which about 1/6th of the
30 aluminium atoms may be replaced with magnesium atoms and with which varying amounts of hydrogen, sodium, potassium, calcium, magnesium and other metals may be loosely combined. The type of bentonite clay which is
35 specifically described herein for making the base beads of the present invention is that which is known as sodium bentonite (or Wyoming or western bentonite), which is normally a light to cream-coloured impalpable powder which, in
40 water, forms a colloidal suspension having strongly thixotropic properties. In water the swelling capacity of the clay will usually be in the range of 3 to 15 ml./gram, preferably 7 to 15 ml./gr. and its viscosity, at a 6% concentration in
45 water, usually be in the range of 3 to 30 centipoises, preferably 8 to 30 centipoises. Preferred swelling bentonites of this type are those which have been sold under the trademark THIOX-JEL, as industrial bentonites, by Benton
50 Clay Company, an affiliate of Georgia Kaolin Co. These materials which are the same as those formerly sold under the trademark THIXO-JEL, are selectively mined and beneficiated bentonites, and those considered to be most useful are those
55 which have been identified as THIXO-JEL's No's 1, 2, 3 and 4. Such materials are of pH's (6% concentration in water) in the range of 8 to 9.4, maximum free moisture contents of about 8% and specific gravities of about 2.6, and for the
60 pulverized grade about 85% passes through a 200 mesh U.S. Sieve Series sieve (200 mesh has openings of 74 microns). Such materials exhibit an exchangeable calcium oxide percentage in the range of about 1 to 1.8 and with respect to
65 magnesium oxide such percentage is normally in

the range of 0.04 to 0.41. Typical chemical analyses of such materials are from 64.8 to 73.0% of SiO_2 , 1.4 to 1.8% of Al_2O_3 , 1.6 to 2.7% of MgO , 1.3 to 3.1% of CaO , 2.3 to 3.4% of Fe_2O_3 , 0.8 to 2.8% of Na_2O and 0.4 to 7.0% of K_2O .
70 Although such bentonites are preferred, equivalent materials from other sources may be substituted.

The polyacrylate, present in preferred base
75 beads of this invention, is a low molecular weight polyacrylate, such molecular weight usually being within the range of about 1,000 to 5,000, preferably 1,000 to 3,000, and most preferably 1,000 to 2,000, or about 2,000. The polyacrylate
80 may be partially neutralized or completely neutralized, e.g., about 1/2 or 1/3 Na salt. Although modified polyacrylates may be substituted for the described sodium polyacrylate, including some other alkali metal polyacrylates,
85 and hydroxylate polyacrylates, it is preferred that such substitutions be limited to a minor proportion of the material and preferably the polyacrylate will be an unsubstituted sodium polyacrylate. Such materials are available from
90 Alco Chemical Corporation under the name Alcosperse (Registered trademark). The sodium polyacrylates are available as clear liquids or powders, with the solutions being of about 25 to 40% solids content, e.g., 30% and with the pH of
95 such solutions or of a 30% aqueous solution of the powder being in the range of about 7.5 to 9.5 e.g., about 9. Such materials are completely soluble in water and have been employed as dispersants. They have been shown to possess
100 the capability of binding calcium ions and have been used to prevent depositing out of insoluble calcium compounds from aqueous solutions.

The presence of the polyacrylate, even in very small quantity, helps to better mix the various
105 crutcher mix components, including, in preferred formulations, ultramarine blue, which, when poorly distributed, can stain laundry washed with detergent made from the base beads. The polyacrylate also helps to evenly distribute any
110 fluorescent brightener throughout the crutcher mix and the detergent composition, thereby aiding the uniform brightening of the wash. Additionally, the polyacrylate makes the total end product (except for the nonionic detergent
115 content) more homogeneous. Processing aids which may be present to prevent gelation and setting of the inorganic materials in the crutcher during mixing and standing thereof are more uniformly dispersed in the crutcher mix, increasing their efficiency of operation. The
120 polyacrylate helps to make the base beads produced by spray drying more absorptive of the liquid state nonionic detergent which may be sprayed onto the beads. In some cases it
125 increases the detergent holding capacity of the beads, while still allowing them to flow freely. Spray drying operations are improved due to less of the sprayed material adhering to the dryer walls, thereby increasing spray tower throughput

rates and diminishing the number of cleanouts required.

The only other material necessary for making the present beads is water, and during drying of the beads the moisture content thereof may be decreased so that the product is almost anhydrous. While it is preferred to employ deionized water, so that the hardness ion contents thereof may be very low and so that metallic ions that can promote decomposition of any organic materials which may be present in the final beads and detergent are minimized, normally city or tap water may be used instead. Normally the hardness content of such water will be less than 150 ppm, as CaCO_3 , more preferably the hardness content will be less than 100 ppm and most preferably it will be less than 50 ppm. Because fairly concentrated aqueous crutcher mixes of silicate, carbonate bicarbonate, zeolite and bentonite and/or polyacrylate present, may "freeze" in the crutcher due to interactions of the components thereof, if held beyond a permissible time, processing aids are preferably present in the crutcher when silicate is present, and consequently, in the finished base beads and detergent composition, to prevent premature solidification or gelation of the mix. Most preferably, such include citric acid and magnesium sulphate. Instead of citric acid, soluble citrates, such as sodium citrate, may be used and while it is preferable to employ anhydrous magnesium sulphate, various hydrates thereof, such as epsom salts, may also be used. Also, magnesium citrate can be substituted. The use of magnesium and citrate ions form the subject matter of our copending British Patent application No. 8129188. In place of the preferred anti-gelling system other means and suitable systems for maintaining the crutcher mix fluid may be substituted, such as sodium sesquicarbonate, employed in replacement of some of the sodium carbonate and sodium bicarbonate. The use of sodium sesquicarbonate forms the subject matter of our copending British patent application No. 8131798.

Various adjuvants, such as perfumes, enzymes, colourants, bleaches and flow promoting agents may often be sprayed onto or otherwise mixed with the base beads after the manufacture thereof, with the nonionic detergent or separate from it, so that they are not adversely affected by the spray drying operation and also, so that their presence in the spray dried beads does not inhibit absorption of nonionic detergent. However, for stable and normally solid adjuvants, mixing in with the inorganic salts slurry in the crutcher is also feasible. Thus, it is contemplated that colouring agents and fluorescent brightener will normally be present in the crutcher mix from which the present base beads are sprayed. The preferred colouring agent is ultramarine blue but other stable pigments and dyes may be used with it or in replacement of it. Among the fluorescent brighteners the most preferred is Tinopal (Registered trademark) 5BM. However, various

other cotton brighteners, such as those sometimes referred to as CC/DAS brighteners, derived from the reaction product of cyanuric chloride and disodium salt of diaminostilbene disulphonate acid, may also be employed, including variations thereof with respect to substituents on the triazine and aromatic rings. This class of brighteners is known in the detergent art and will most often be used when bleaching components are not present in the final product. In such instances bleach stable brighteners may be employed. Among these may be mentioned the benzidine sulphone disulphonic acids, naphthotriazolyl stilbene sulphonic acids and benzimidazolyl derivatives. Polyamide brighteners, which also may be present, include aminocoumarin or diphenyl pyrazoline derivatives, and polyester brighteners, which can also be used, include naphthotriazolyl stilbenes. All such brighteners are normally used as their soluble salts but they may also be charged as the corresponding acids. The cotton brighteners will usually comprise major proportions of the brightener systems.

Of the materials that may be post-added to the spray dried base beads the most important, of course, is the nonionic detergent. Although various nonionic detergents of satisfactory physical characteristics may be utilized, including condensation products of ethylene oxide and propylene oxide with each other and with hydroxyl-containing bases, such as nonyl phenol and Oxo-type alcohols, it is usually preferred that the nonionic detergent be a condensation product of ethylene oxide and higher fatty alcohol. In such products the higher fatty alcohol is of 10 to 20 carbon atoms, preferably 12 to 16 carbon atoms, and the nonionic detergent contains from about 3 to 20 ethylene oxide groups per mol, preferably from 6 to 12. Such detergents are made by Shell Chemical Company and are available under the trade names Neodol (Registered trademark) 23—6.5 and 23—7.

The enzyme preparations, which normally are postadded to the base beads, may be any of a variety of commercially available products, included among which are Alcalase (Registered trademark), manufactured by Novo Industri, A/S, and Maxatase (Registered trademark), both of which are alkaline proteases (subtilisin). Although the alkaline proteases are preferred, amylolytic enzymes, such as alphaamylase, as well as proteolytic enzymes, may be utilized. The mentioned compositions usually contain active enzymes in combination with an inert powdered vehicle, such as sodium or calcium sulphate, and the proportion of active enzyme may vary widely, usually being from 2 to 80% of the commercial preparation. The perfumes employed, which are usually heat sensitive and may include some volatile solvent material, such as alcohol, are normally of synthetic perfumery materials, sometimes mixed with natural components, and generally will include alcohols, aldehydes, terpenes, fixatives and other normal perfume

components. Flow promoting agents, such as special clays, which are sometimes added to detergent products, while often useful to improve flowability and to diminish tackiness of various components, are unnecessary in the present cases, possibly in part due to the presence of the bentonite and/or polyacrylate. However, they may be added if desired, to further increase flowability.

The proportions of the various components in the base beads will be such as to result in their being freeflowing and sufficiently absorptive of a nonionic detergent applied thereto in liquid state so that the detergent composition made from them by incorporation of such detergent will also be satisfactorily free-flowing. Also, of course, the detergent composition made from the base beads must be an effective cleaning agent, with the builders present acting to assist the organic detergent in aqueous solutions of the composition, and it is important that the resulting product be one which does not cause objectionable deposition of zeolite particles (possibly with other substances, such as normally water soluble silicates) on washed materials. It has been found that fairly satisfactory base beads to accomplish this purpose, when silicate is present, may comprise, by weight from 15 to 30% of sodium carbonate, 10 to 22% of sodium bicarbonate, 20 to 40% of water softening aluminium silicate (zeolite), 3 or 4 to 12% of sodium silicate and 1 to 15% of bentonite, as the active components, and 1 to 15% of water. In such beads the aluminium silicate will preferably be a sodium zeolite containing from 15 to 25% of weight thereof of water of hydration and more preferably, such zeolite will be Zeolite A. The preferred weight ratio of sodium carbonate:sodium bicarbonate in the product is within the range of about 1 to 3, the beads made have a bulk density in the range of 0.6 to 0.9 gr/cc., more preferably 0.7 to 0.8 gr/cc, and the base particle sizes are in the range of No's 10 to 100 (through No. 10 and on.No. 100), U.S. Sieve Series, more preferably 10 to 60, U.S. Sieve Series. 100 mesh has openings of 149 microns, 10 mesh has openings of 2000 microns (2 mms), and 60 mesh has openings of 250 microns. Further preferred proportions of components are from 20 to 25% of sodium carbonate, 13 to 19% of sodium bicarbonate, 30 to 37% of hydrated zeolite, 5 to 8 or 10% of sodium silicate, 5 to 8% of bentonite and 4 to 10% of water, exclusive of the water of hydration of the zeolite. In such more preferred products the weight ratio of sodium carbonate:sodium bicarbonate is within the range of 1:1 to 2:1.

When a polyacrylate is present together with the zeolite in the base bead composition the proportion thereof will normally be in the range of 0.1 to 2%, preferably 0.2 to 1.6% and more preferably 0.8 to 1.4%. Proportions of adjuvants and processing aids and fillers, if any, in the base beads, will normally be limited to 20% thereof, preferably being 1 to 10% and more preferably being 3 to 7% thereof. The proportions of

processing aids, when magnesium sulphate and citric acid are employed, will normally be from 1 to 3% of magnesium sulphate, more preferably 1.5 to 2.5% thereof, and 0.2 to 1% of sodium citrate, more preferably 0.2 to 0.5% thereof. With respect to pigmenting and fluorescent brightening agents the proportions will preferably be from 0.05 to 0.6% of pigment, such as ultramarine blue, more preferably 0.2 to 0.4%, and 0.1 to 4% of fluorescent brightener, more preferably 1 to 1.5 to 3% thereof. Such proportions of processing aids and adjuvants apply to the various types of beads of this invention, when such aids or adjuvants are employed.

The proportions of the various components in the crutcher mix and in the base beads when making beads comprising polyacrylate but omitting bentonite will be such as to result in the mix being uniform or nearly so, and the beads being free-flowing and sufficiently absorptive of a nonionic detergent applied thereto in liquid state so that the detergent composition made from them by incorporation of such detergent will also be satisfactorily free-flowing. It has been found that satisfactory base beads to accomplish this purpose comprise, by weight, from 15 to 30% of sodium carbonate, 10 to 22% of sodium bicarbonate, 20 to 40% of water softening aluminium silicate (zeolite), 3 or 4 to 18% of sodium silicate and 0.1 to 2% of polyacrylate, as the active components, and 1 to 12 or 15% of water. The preferred weight ratio of sodium carbonate:sodium bicarbonate in the product is within the range of about 1:1 to 3:1, the beads made have a bulk density in the range of 0.5 to 0.8 gr/cc, preferably 0.7 to 0.8 gr/cc, and the bead particle sizes are in the range of No's 10 to 100 (through No. 10 and on No. 100), U.S. Sieve Series, more preferably 10 to 60, U.S. Sieve Series. Further preferred proportions of components are from 20 to 25% of sodium carbonate, 13 to 19% of sodium bicarbonate, 30 to 37% of hydrated zeolite, 7 to 15% of sodium silicate, 0.5 to 1.5% of sodium polyacrylate and 3 to 10% of water, exclusive of the water of hydration of the zeolite. In more preferred products of such type the weight ratio of sodium carbonate:sodium bicarbonate is within the range of 1:1 to 2:1.

When the beads to be made will have little or no water soluble silicate present, as was previously indicated when referring to other types of the beads of the present invention, the proportions of the various components in the base beads will be such as to result in their being free-flowing and sufficiently absorptive of a nonionic detergent applied thereto in liquid state so that the detergent composition made from them by incorporation of such detergent will also be satisfactorily free-flowing. Also, it is important that the resulting product be one which does not cause objectionable deposition of zeolite particles (possibly with other substances) on washed materials. It is also desirable for the base beads made to be of appropriate bulk density and colour.

It has been found that satisfactory such base beads to accomplish these purposes comprise, by weight, from 15 to 30% of sodium carbonate, 10 to 22% of sodium bicarbonate, 10 to 50% of water softening aluminium silicate (zeolite), 0 to 3% of sodium silicate and 3 to 20% of bentonite, as the active components, and 1 to 15% of water. The percentage of water given is free water and does not include the water of hydration of the zeolite. Correspondingly, the percentage of zeolite does include water of hydration. In some instances the product may be anhydrous, with respect to free moisture content, but such cases are rare and it is normally desirable for at least a small proportion of water to be in the base beads to prevent undesirable powdering thereof, which could sometimes otherwise occur with particular anhydrous formulas. The preferred weight ratio of sodium carbonate:sodium bicarbonate in the product is within the range of about 1:1 to 3:1, the beads made have a bulk density in the range of 0.6 to 0.9 gr/cc, more preferably 0.6 to 0.7 to 0.8 gr/cc., and the bead particle sizes are in the range of No's 10 to 100 (through No. 10 and on No. 100), U.S. Sieve Series, more preferably 10 to 60 U.S. Sieve Series. Further preferred proportions of components are from 20 to 27% of sodium carbonate, 14 to 21% of sodium bicarbonate, 20 to 50% of hydrated zeolite, 0% of sodium silicate, 5 to 20% of bentonite and 1 to 5% of water, exclusive of the water of hydration of the zeolite. In such more preferred products the weight of sodium carbonate:sodium bicarbonate is within the range of 1:1 to 2:1. When silicate is present in such base beads it will be preferred to limit its content to 2%, more preferably to 0.5 to 1%. Other preferred ranges of proportions of important components of this invention are 35 to 45% of hydrated zeolite and 5 to 15%, more preferably 10 to 15% of bentonite.

When a polyacrylate is present in such base bead composition the proportion thereof will normally be in the range of 0.05 to 0.5%, preferably 0.05 to 0.3%, and more preferably 0.1 to 0.2%. Proportions of adjuvants and processing aids and fillers, if any, in such base beads, will normally be limited to 20% thereof, preferably being 1 to 10% and more preferably being 3 to 7% thereof, and the proportions will be like those previously given.

While it has been found that detergent compositions made from the present base beads do not require the presence of any anti-corrosion additive to replace the silicate, it is within the scope of the present invention to utilize suitable such materials and it will be preferred to employ those which are stable under crutching and spray drying conditions and which do not adversely affect such operations. Such anti-corrosion additives or antioxidants may be organic or inorganic, with inorganic materials normally being preferred, and they will preferably be chosen for suitability for preventing corrosion of aluminium parts of washing machines. If it is desired to continue to utilize a silicate for such

purpose or to employ a silicate for its magnesium ion hardness treatment effect, a powdered silicate will normally be preferable, such as hydrous sodium silicate, which is commercially available under the name Britesil (Registered trademark) manufactured by Philadelphia Quartz Co. ($\text{Na}_2\text{O}:\text{SiO}_2=1:2.4$), and such will be post-added. However, other normally solid soluble silicates, preferably of alkali metals, may also be post-added to the beads of this invention into which nonionic detergent has previously been absorbed.

When it is desired for the product made to possess textile softening characteristics, softening materials, preferably in dry powder form, may also be post-added to the base beads in suitable manner. This class of materials is well-known and most generally such softeners are cationic compounds, particularly quaternary ammonium compounds, such as quaternary ammonium halides. Especially preferred are the higher alkyl, alkylaryl- and arylalkyl-lower alkyl quaternary ammonium chlorides and bromides, such as distearyl dimethyl ammonium chloride. Of commercial softening materials that which is most preferred is sold under the trade name Arosurf (Registered trademark) TA-100, manufactured by Sherex Chemical Company, Inc. Such compounds possess antistatic and antibacterial properties, too, but if desired, other antibacterial adjuvants may also be employed, preferably also incorporated in the product by post-addition.

It is an important feature of the present invention that an effective built detergent composition based on nonionic detergent alone, may be made by a commercially feasible process but sometimes it may be desirable to also have an anionic surface active or detergent component present in the final product, usually for its contribution to the product of foaming characteristics and supplementary cleaning effects. Normally it will be preferred not to incorporate such anionic detergent material(s) in the crutcher, so if such is/are to be employed it will preferable be by post-addition to the spray dried base beads, and normally such post-addition will take place after absorption by the beads of the liquid state nonionic detergent. While various types of anionic detergents, preferably completely in powder form, and/or sometimes mixed with builder-material, may be utilized, those which are preferred are the linear higher alkylbenzene sulphonates, higher alkyl or fatty alcohol sulphonates and polyethoxylated higher fatty alcohol sulphonates. In such products the higher alkyl and higher alcohol portions will normally be of 8 to 20, preferably 12 to 16 carbon atoms, and the detergents will be present as their water soluble alkali metal salts, preferably as sodium salts. The ethoxylated alcohol sulphate will normally contain from 3 to 20 mols of ethylene oxide per mol of fatty alcohol. The ranges of proportions of the various bead components in the final detergent composition may readily be calculated from those given for the base beads,

diminished by proportions of detergent and other materials post-added to the beads. Thus, if the final detergent composition had only nonionic detergent added to it so that the final product contains 20% of nonionic detergent, from the various ranges given for components in the base beads range of proportions thereof may be calculated by multiplying by 0.8, which is $(100 - 20)/100$. Similarly, when the proportion of non-ionic detergent (in formulas wherein it is the only additive to the beads) may range from 8 to 25% of the detergent composition, the multipliers will be from 0.75 to 0.92. Usually the final percentage of nonionic detergent in the product will be in the 8 to 25% range, preferably being 15 to 22% and more preferably being about 20%, but in some situations, for certain types of products, proportions in the 8 to 13% range may be preferred. Normally the percentage of perfume in the final product will be in the range of 0.1 to 1%, preferably 0.2 to 0.4%, the percentage of enzyme will be from 0.5 to 3%, preferably 1 or 1.5 to 2.5% and the percentage of flow improving agent, which may be post-added, will be less than 2%, preferably less than 1%. Of course, to calculate the ranges of bead components in the final composition, in addition to basing such calculations on the percentage of nonionic detergent in the final product (post-added) the percentages of other post-adjuvants will also have to be considered. Also, if some post-additions are made by means of aqueous solutions of the additives, this will affect the moisture content too, which will often be kept in the 1 to 12%, range but sometimes may be extended to 15%.

When polyacrylate is employed and bentonite is omitted, the ranges of proportions of the various detergent composition components are preferably 13 to 28% of sodium carbonate, 8 to 18% of sodium bicarbonate, 15 to 25% of water softening aluminium silicate, 3 to 40% of sodium silicate, 0.1 to 1.6% of polyacrylate, 8 to 30% of nonionic detergent and 1 to 10% of water. Preferably, such ranges are 16 to 21% of sodium carbonate, 10 to 15% of sodium bicarbonate, 22 to 32% of hydrated zeolite, 8 to 13% of sodium silicate, 0.5 to 1.5% of sodium polyacrylate, 3 to 6% (and sometimes 3 to 10%) of moisture and 10 to 22 or 25% of nonionic detergent. The processing aids, brightener and colourant percentages in the final detergent composition will be approximately the same as in the base beads, preferably being in the range of 0.2 to 0.6% for sodium citrate (resulting from the addition of citric acid) and 1 to 2% of the magnesium sulphate, 0.1 to 0.3% for the ultramarine blue and 1.5 to 2% for the fluorescent brightening agent. The enzyme content will be in the 0.5 to 3% range, usually being 1 to 2%, and the perfume content will be 0.1 to 1%, preferably 0.2 to 0.4%.

The ranges of proportions of the various bead components in the spray dried part of the final detergent composition, when little or no silicate is

present, may be calculated in the manner previously described. As to post-added components, the percentages of nonionic detergent will be the same as given earlier, the percentage of perfume in the final product will be in the range of 0.1 to 1%, preferably 0.2 to 0.4%, the percentage of enzyme will be from 0.5 to 3%, preferably 1 to 2%, and if a hydrous silicate is post-added the proportion thereof will normally be from 2 to 10%, preferably 3 to 8%, e.g. about 5%. When a softening compound is present in the final product the proportion thereof will normally be in the range of 3 to 12%, preferably 5 to 10%, and when anionic detergent(s) is/are utilized, the proportion thereof will be limited to no more than that of the nonionic detergent and the total weight of anionic and nonionic detergents in the final product will be within the ranges previously given for nonionic detergent alone. If anionic detergent is employed, the amount thereof present will normally be within the range of 0.2 to 0.8 times the weight of the nonionic detergent. Of course, to calculate the ranges of bead components in the final composition, in addition to basing such calculations on the percentage of nonionic detergent in the final product (post added) the percentages of other post-adjuvants will also have to be considered. Also, if some post-additions are made by means of aqueous solutions of the additives, this will affect the moisture content too, but such will usually be kept in the 1 to 12% range for the final product, which sometimes may be extended to 15%.

The base beads of the invention are spray dried from an aqueous crutcher mix which normally will contain from about 40 to about 70 or 75% of solids, preferably 50 to 65% thereof, with the balance being water, preferably deionized water as previously described, but city water may also be employed. The crutcher mix composition ranges may be calculated back from the desired base beads composition ranges on the basis of the moisture contents of the beads and the mix. Thus, for example, in a crutcher mix to contain 50% of moisture, from which mix a base bead containing 5% moisture is to be produced (neglecting water of hydration in the zeolite), the percentages of components in the base bead should be multiplied by $10/19$, which is $(100/2(100-5))$. The above calculations are satisfactory for components which do not decompose in the spray drying operation but it is known that a portion of the bicarbonate changes to carbonate when dried at elevated temperatures in a spray tower. Accordingly, knowing the characteristics of the tower and the drying conditions, so that the extent of bicarbonate decomposition is predictable, one can calculate the proportion of carbonate and bicarbonate to have in the crutcher mix. Thus, for example, when it is desired to make a product containing about 22% of sodium carbonate and about 16% of sodium bicarbonate, in those cases wherein about one-third of the bicarbonate decomposes to carbonate in the spray tower (with two parts of

carbonate resulting from three parts of decomposed bicarbonate), one might charge 24% bicarbonate and 17% carbonate to the crutcher (dry basis).

5 With respect to the various formulations and calculations it will be considered that the zeolite in the crutcher mix and in the spray dried base beads and detergent composition is hydrated to the extent of about 20% water of hydration but it is
10 recognized that the degree of hydration might vary. However, for consistency and for the purpose of such calculations such constant degree of hydration will be assumed.

The crutcher mix from which the base beads of
15 the present invention are most preferably made by spray drying is one which is primarily inorganic and the content of organic material is usually limited to 10%, preferably to 7%, and more preferably to 4%, on a solids basis. Among such
20 organic materials which may be present are citric materials (citric acid and soluble citrates), fluorescent brightener, polyacrylate, dyes and pigments. Other organic materials may also be present, including hydrotropic salts, chelating
25 agents and polyelectrolytes, but, as is evident, the crutcher mix will remain primarily of inorganic materials and water.

For the polyacrylate-containing beads, without bentonite, on a 100% solids basis, the crutcher
30 mix will normally be about 10 to 25% of sodium carbonate, 15 to 30% of sodium bicarbonate, with the weight ratio of sodium bicarbonate:sodium carbonate being within the range of 0.5:1 to 2:1, 20 to 40% of water
35 softening aluminium silicate, 4 to 18% of sodium silicate and 0.1 to 2% of polyacrylate. When processing aids are present the proportions thereof, on the same basis, will usually be from 1 to 3% of magnesium sulphate and 0.2 to 1% of
40 sodium citrate. Preferably, in such crutcher slurries, the content of sodium polyacrylate will be from 0.5 to 1.5% and, when processing aids and colourants are also present the proportions thereof will be from 1.5 to 2.5% of magnesium
45 sulphate, 0.2 to 0.5% of sodium citrate, 0.2 to 0.4% of ultramarine blue and 1.5 to 3% of fluorescent brightening agent, on a solids basis.

The crutcher mix is preferably made by sequentially adding various components thereof
50 in the manner which will result in the most miscible, readily pumpable and non-setting slurry for spray drying. The order of addition of the various components may be varied, depending on the circumstances, but it is highly desirable to
55 add the silicate solution (if any) last, and if not last, at least after the addition of any gel or set preventing combination of materials or processing aids. Normally it is preferable for all or almost all of the water to be added to the crutcher first,
60 preferably at about the processing temperature, after which the processing aids (if present) and other minor components, including pigments and fluorescent brighteners, and polyacrylates (if present), are added, followed by the bentonite (if
65 present) zeolite, bicarbonate, carbonate and

silicate (if present). Usually during such additions each component will be mixed in thoroughly before addition of the next component but methods of addition may be varied, depending on
70 the circumstances, so as to allow co-additions when such are feasible. Sometimes component additions, such as silicate additions, may be in two or more parts. Different components may be pre-mixed before addition, to speed the mixing
75 process. Normally, mixing speed and power will be increased as the materials are added. For example, low speeds may be used until after admixing in of the last of the bentonite or zeolite, after which the speed may be increased to
80 medium and then to high, before, during and after addition of any silicate solution.

The temperature of the aqueous medium in the crutcher will usually be about room temperature or elevated, normally being in the 20 to 80°C
85 range, preferably from 30 to 75°C and more preferably, 40 to 70°C. Heating the crutcher medium may promote solution of the water soluble salts of the mix and thereby increase miscibility but the heating operation, when
90 effected in the crutcher, can slow production rates, and can promote setting of the mix. Therefore, an advantage of having processing aiding materials present in the mix is that they ensure that the desirable non-gelling slurries will
95 result at both lower and higher temperatures. Temperatures higher than 80°C (and sometimes 70°C) will usually be avoided because of the possibility of decomposition of one or more crutcher mix components, e.g. sodium
100 bicarbonate. Also, in some cases, lower crutcher temperatures increase the upper limits of crutcher solids contents, probably due to insolubilizing normally gelling or setting components.

Crutcher mixing times to obtain good slurries
105 can vary widely, from as little as five minutes in small crutchers and for slurries of higher moisture contents, to as much as four hours, in some cases. The mixing times needed to bring all the crutcher mix components substantially
110 homogeneously together in one medium may be as little as ten minutes but in some case can take up to an hour, although 30 minutes is a preferable upper limit. Counting any such initial admixing times, normal crutching periods will be from 15
115 minutes to two hours, e.g., 20 minutes to one hour, but the crutcher mix should be such as to be mobile, not gelled or set, for at least one hour, preferably for two hours, and more preferably for
120 four hours or longer, after completion of the making of the mix, and may even be mobile for as much as 10 to 30 hours before pump-out to the spray tower, for situations wherein other manufacturing problems may be encountered.

The crutched slurry, with the various salts and
125 any other components thereof dissolved or in particulate form, uniformly distributed therein, is transferred in usual manner to a spray drying tower, which is normally located near the crutcher. The slurry is dropped from the bottom of
130 the crutcher to a positive displacement pump,

which forces it at high pressure through spray nozzles at the top of a conventional spray tower (countercurrent or concurrent), wherein the droplets of the slurry fall through a hot drying gas, usually the combustion products of fuel oil or natural gas, in which the droplets are dried to desired absorptive bead form. During the drying part of the bicarbonate (often 1/4 to 1/2, e.g., 1/3) may be converted to carbonate, with the release of carbon dioxide, which, in conjunction with the content of polyacrylate which may be present in the mix being spray dried, can improve the physical characteristics of the beads made, so that they become more absorptive of liquids, such as liquid nonionic detergent, which may be post-sprayed onto them subsequently. However, zeolite and bentonite components of base beads made also appear to favour absorption of liquid, and the polyacrylate also promotes faster drying, thereby increasing tower throughput.

After drying, the product is screened to desired size, e.g. 10 to 60 or 100, U.S. Sieve Series, and is ready for application of nonionic detergent spray thereto, with the beads being either in warm or cooled (to room temperature) condition. However, the nonionic detergent will usually be at an elevated temperature, such as 30 to 60°C, e.g., 50°C, to assure that it will be liquid; yet, upon cooling to room temperature, desirably it will be a solid, often resembling a waxy solid. Even if at room temperature the nonionic detergent is somewhat tacky, this characteristic does not make the final composition poorly flowing because the detergent penetrates to below (or within) the bead surface. The nonionic detergent, is preferably applied to the beads whilst they are moved or tumbled e.g. in known manner, as a spray or as droplets. The nonionic detergent is preferably a condensation product of ethylene oxide and higher fatty alcohol, such as was previously described, but other nonionics may also be operative. The enzyme preparation (herein referred to as enzyme, although it is recognized that it includes a carrier material, too), hydrous silicate and any other powdered adjuvants to be post-added may be dusted onto the detergent particles, and perfume and any other liquids may be sprayed on at a suitable point, before or after addition(s) of the powder(s).

The spray dried base beads and the detergent compositions made from them may include little or no silicate from the crutcher mix and in such case silicate in solid form may be post-added. The post-added powdered silicate, if employed, does not seem to react with the zeolite as much, so zeolite-silicate agglomerations that tend to deposit on laundered articles are reduced. Although, without the bentonite being present, silicate would normally be used, at least for its anti-corrosion effects, the present detergent compositions have not been found to corrode aluminium articles, even without the silicate. Furthermore, bentonite does not adversely affect the stability of the product and in fact, appears to help to hold the beads together, making them

resistant to crushing and powdering during shipment and use. The presence of bentonite and/or polyacrylate significantly improves the properties of the final detergent composition, with the bentonite producing higher calcium ion binding rates and resulting in less zeolite being deposited on laundered fabrics. When the low molecular weight polyacrylate is present the beads become more porous and better absorb the nonionic detergent in liquid state, without unduly lowering the bulk density of the product. Considering that bentonite is a clay and might be expected to create deposition and gelation problems of its own, the lowered deposition of zeolites and absence of gelation are surprising, and are important results of the present invention.

The present invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples, some of which are comparative. Unless otherwise indicated all temperatures are in °C, and all parts are by weight in the examples and throughout the specification. Also, when weights and proportions of zeolite are given these are intended to be for the normal hydrate being used, because it is considered that the zeolite water of hydration does not leave the zeolite and does not become part of the aqueous solvent medium in the present crutching operations, and also because some of the water present in the base beads and the detergent compositions is present as water of hydration of the zeolite.

Examples 1A to 1E

100 Example 1A — Preparation of crutcher mix.

A 456 kg batch of crutcher mix for spray drying to base beads of this invention and conversion to a detergent composition was made by adding to the crutcher 1832 kg of deionized water at a temperature of about 27°C, and sequentially and with low speed crutcher mixing, admixing with it 51.3 kg of anhydrous magnesium sulphate, (105.5 kg of epsom salts may be used instead, in which situation the water charged initially will be reduced to 1777.4 kg), 12.7 kg of citric acid, 57.6 kg of Tinopal 5BM extra Conc. (CIBA-Geigy), 68 kg of ultramarine blue powder, 169.6 kg of Thixo-Jel No. 1 (bentonite) 914 kg of Linde hydrated Zeolite 4A (20% water of crystallization), 636.9 kg of sodium bicarbonate and 456.3 kg of sodium carbonate (soda ash). The mixer speed is then increased to high (in some cases it may be increased to medium speed at an earlier time if the mix is not blending as well as desired) and 189.6 kg of sodium silicate of (Na₂O:SiO₂ ratio of 1:2.4) were admixed (as 399.2 kg of 47.5% of aqueous solution). Mixing of the entire batch then continued for about an hour (in some cases as long as four hours mixing may be used), during which time about 90.7 to 272.2 kg of water may be lost by evaporation, which water may be replenished if desired. During the mixing time the crutcher slurry was continuously mobile and did not gel, set or cake. Because bicarbonate partially

decomposes to carbonate during spray drying, the amounts thereof may be varied, depending on the spray tower operating characteristics.

Example 1B — Spray drying of base beads

Starting about five minutes after all components of the crutcher mix were present, the mix of Example 1A was dropped from the crutcher to a pump, which pumped it at a pressure which was about 21 kg/sq cm into the top of a countercurrent spray tower wherein the initial temperature was about 430°C and the final temperature was about 105°C. The essentially inorganic base beads resulting were of a bulk density of about 0.6 to 0.7 gr/ml, a percentage initial adhesion approximating 40%, of particle size range substantially between 10 and 100 mesh U.S. Sieve Series (they are screened to such range), and of a fines characteristic (through U.S. Sieve No. 50 which has openings of 297 microns) of about 15%. The moisture content of the beads was about 7%. The base beads were found to be free-flowing, non-tacky, satisfactorily porous, yet firm on the surfaces thereof, and were capable of readily absorbing significant proportions of liquid nonionic detergent without becoming objectionably tacky.

Example 1C — Preparation of detergent product

Detergent products were made from the spray dried beads of Example 1B by spraying onto the tumbling bead surfaces thereof a normally waxy nonionic detergent, either Neodal 23—6.5 or Neodol 23—7, in heated liquid state, in such quantity as to result in a final product containing 20% of nonionic detergent, and proteolytic enzyme (Alcalase) was applied in powdered form to result in a 1.99% concentration in the product. Perfume was sprayed onto the product to produce a 0.25% concentration therein. The resulting detergent products were of a bulk density of about 0.7 to 0.8 gr/ml and contained 27.3% of zeolite (hydrated), 20.1% of nonionic detergent, 17.8% of sodium carbonate (some of which was produced by decomposition of sodium bicarbonate), 12.7% of sodium bicarbonate, 5.6% of sodium silicate, 5.45% of water, 2.0% of enzyme, 1.7% of fluorescent brightener, 1.5% of magnesium sulphate, 0.4% of citric acid (in citrate form), 0.25% of perfume, 0.2% of ultramarine blue, 5.0% of bentonite (Thixo-Jel)

The detergent made, of the above formula, was an excellent heavy duty laundry detergent and was especially useful for washing household laundry in automatic washing machines. It was physically and aesthetically advantageous and attractive because it is non-dusting and extremely freely flowing, which allows it to be packaged in narrow-necked glass and plastic bottles, from which it flows readily for dispensing. The detergent compositions of the invention, containing bentonite, as described, are found to be of significantly improved calcium ion binding rates but more importantly, they leave less

residue on laundry washed with them (in an automatic washing machine at usual concentrations for such product and at normal washing temperatures) than do similar compositions not containing the bentonite. This difference is accentuated when the wash water is high in hardness, e.g., 200 ppm, as calcium carbonate, the wash water is cold, and a gentle agitation cycle is employed.

Example 1D

In a control experiment base beads were made in which the bentonite was omitted from the crutcher mix, being replaced by equal weights of sodium carbonate and sodium bicarbonate, the total of the added materials equalling the weight of the bentonite replaced. The crutcher mix was spray dried and converted to a detergent composition in the same way as described in Examples 1B and 1C. Such "control" product, while useful as a detergent, resulted in more residue being deposited on washed laundry than with the experimental product of the present invention and was of a lower calcium binding rate.

Example 1F

When the content of silicate in the control beads of Example 1D was increased to 10.7%, with sodium carbonate and sodium bicarbonate concentrations being decreased to compensate for the silicate increase, the residue deposition is even worse than with Example 1D.

Following normal procedure, crutcher mixes will be made quickly and may be emptied from the crutcher equally fast, sometimes being made within a period of as little as five minutes and being pumped out of the crutcher in as little as ten minutes. Yet, it is often important that the present mixes to be able to withstand at least an hour in the crutcher without gelling or solidifying because sometimes holdups of such times are encountered in commercial production. The described crutcher mix is capable of being held for as long as four hours and often appreciably longer, without gelling or solidifying, which is attributed, at least in part, to the content of magnesium sulphate and citric acid processing aids therein. However, other processing aids intended to prevent gelation and setting of the crutcher mixes may be substituted, and under some conditions the proportions thereof may be decreased and one or both may be omitted. Similarly, other minor components of the crutcher mix, such as the fluorescent brightener and pigment, may be omitted therefrom and enzyme and perfume may be omitted from the final product, although it is highly preferable for all such materials to be present. The crutcher mix temperature may be modified, as by elevation to 52°C, and the proportions of the various components may be varied $\pm 10\%$, $\pm 20\%$, and $\pm 30\%$, while still maintaining them within the ranges previously given, and workable crutcher mixes that result in the desired beads and detergent compositions will be obtainable.

Instead of employing anhydrous magnesium sulphate an equivalent proportion of epsom salts may be substituted and various other components may be added as aqueous solutions, providing that the amounts of moisture added with them are subtracted from that added to the crutcher. Other orders of addition may be employed but normally it will be desired to have the processing aids added early in the manufacturing procedure, with the silicate being added last or near the end thereof. Instead of using Zeolite 4A, Zeolites X and Y may be substituted, as may be other types of Zeolite A. While it is preferred to employ the hydrated Zeolite 4A of this example, various degrees of hydration of the zeolite are acceptable and in some instances nearly anhydrous crystalline zeolites or amorphous zeolites may be employed. Varying the amount of bentonite within the range given, to 3% to 10%, for example, still results in useful products but those containing larger proportions of bentonite will usually be more effective in preventing zeolite deposition on laundry. However, the proportion employed commercially depends on a number of factors and normally will represent a balance struck between the desired diminution of zeolite residue and the desired building and other functional effects of other detergent composition components.

Example 2A to 2C Example 2A

A product like that of Example 1A was made but with the addition of low molecular weight polyacrylate (MW=1,000 to 2,000) in the crutcher mix, added early in the production thereof, before the bentonite, so as to result in a comparable product containing 1% of the polyacrylate (Alcosperse 107D). The only formula change to compensate for the addition of the polyacrylate was a decrease in the sodium bicarbonate content in the crutcher mix by an equal weight. Additionally, the batch made was smaller, using a pilot plant crutcher.

Example 2B

Base beads were made by spray drying the mix of Example 2A in the same manner as previously described in Example 1B.

Example 2C

The beads of Example 2B were converted to a final detergent product of the same type as in Example 1C with the exception of the addition of the polyacrylate. The composition was tested and the properties thereof were observed. It was found to be an excellent free flowing detergent, with less zeolite residue on washed laundry than controls of the types mentioned in Example 1D and 1F. Additionally, the presence of the Alcosperse noticeably improved the absorption characteristics of the beads made so that they more readily absorbed liquid nonionic detergent, which may be of the ethoxylated alcohol type or other types mentioned in the specification. Yet

the bulk densities of the beads and the product were not lowered appreciably, which is significant when it is desired to manufacture a comparatively high bulk density, concentrated particulate detergent. It has been observed that when the described polyacrylate is present in the crutcher mix better spray drying operations result and less material is lost by deposition on the spray tower walls, which processing advantages are important in speeding commercial production and in avoiding waste reworking of off-grade material.

As with Example 1, the proportions of components in this example may also be varied, within the limits given in the specification, to produce base beads and detergent compositions of improved properties. While it appears that about 1% of the described polyacrylate is an optimum proportion to utilize in the detergent compositions, from 0.1 to 2% thereof will have good effects, with use of the greater proportions resulting in greater porosity improvements of the beads. For example, instead of 1%, 0.5% and 1.5% are also desirable proportions of the polyacrylate. In some cases it may be desirable to utilize polyacrylates of higher molecular weights within the ranges given, e.g., 4,000—5,000, but in most cases the lower portion of the range will be preferred. As with Example 1, in some instances processing aids, perfume, enzyme, fluorescent brightener and pigment may be omitted or changed but in all such instances the mentioned zeolite, carbonate, bicarbonate, silicate and bentonite, together with polyacrylate, will be present in the given proportions in the base beads, and nonionic detergent will also be present in the final detergent composition, which, like the others, is of the non-phosphate type.

Example 3A to 3C Example 3A

Using pilot plant equipment, detergent base beads were made comprising 23.37% of sodium carbonate, 16.60% of sodium bicarbonate, 34.74% of zeolite 4A, 13.64% of sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:2.4), 0.26% of ultramarine blue, 2.20% of Tinopal 5BM Extra Conc. (CIBA Geigy), 1.95% of magnesium sulphate, 0.32% of citric acid, (present as sodium citrate), 1.29% of sodium polyacrylate of molecular weight in the range of 1,000 to 2,000 (Alcosperse 107D) and 5.64% of moisture. Such a product was made from a pilot plant crutcher batch containing 50% solids and 50% water, including water added in the aqueous silicate solution, with the polyacrylate (as when an aqueous solution thereof, such as Alcosperse 107 is utilized) and with epsom salts, if used. The other solid components comprise the other 50% of the crutcher mix and were present in the same relative proportions as given above with the exception of the sodium carbonate and sodium bicarbonate, in which cases, assuming 1/3 decomposition of the bicarbonate to carbonate, 24.90 parts of sodium bicarbonate

(proportionately) and 17.8 parts of sodium carbonate (proportionately) were employed.

The water charged to the crutcher was deionized water and it was at a temperature of 27°C. The magnesium sulphate charged was anhydrous, although an equivalent proportion of epsom salts may be used instead. After charging of the water the magnesium sulphate, citric acid, Tinopal 5BM Extra Conc, ultramarine blue powder and Alcosperse 107D were added to the crutcher, normally with the mixer at relatively slow speed, after which the Linde hydrated zeolite 4A (20% water of crystallization), sodium bicarbonate and sodium carbonate may be charged, with the mixer at slow speed or medium speed. The mixer speed was then increased to high and the sodium silicate was added as a 47.5% aqueous solution. Mixing of the entire batch then continued for about an hour (in some cases as long as four hours mixing may be employed), during which time an appreciable proportion of water, sometimes 2 to 6%, may be lost by evaporation. Such water may be replenished, if desired. During the mixing time the crutcher slurry was continuously mobile and did not gel, set or cake.

Because bicarbonate decomposition may vary depending on spray drying conditions the amount of bicarbonate and carbonate charged may also be varied accordingly to obtain the desired base bead composition.

Example 3B

Starting about five minutes after all the components of the crutcher mix were present, the mix of Example 3A was dropped from the crutcher to a pump, which pumped it at a pressure which was maintained to be about 21 kg/sq cm into the top of a countercurrent spray tower wherein the initial temperature was about 430°C, and the final temperature was about 105°C. The essentially inorganic base beads resulting were of a bulk density of about 0.6 to 0.7 gr/ml, low percentage initial adhesion, of particle size range substantially between 10 and 100 mesh, U.S. Sieve Series (they are screened to such range), and did not include an objectionable proportion of fines. The moisture content of the beads was about 5.6%. The base beads were found to be free flowing, non-tacky, satisfactorily porous and yet of desired physical strength, and were capable of readily absorbing increased proportions, e.g., 2 to 5% more of liquid nonionic detergent sprayed onto them, without becoming objectionably tacky. The spray dried beads comprised 23.37% of sodium carbonate, 16.60% of sodium bicarbonate, 34.74% of zeolite 4A, 13.64% of sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:2.4), 0.26% of ultramarine blue, 2.20 of Tinopal 5BM Extra Conc. (CIBA Geigy), 1.95% of magnesium sulphate, 0.32% of citric acid (present as sodium citrate), 1.29% of sodium polyacrylate of molecular weight in the range of 1.000 to 2.000 (Alcosperse 107D) and 5.64% of moisture. In addition to the desirable properties of the base beads made, it was noted that the buildup of product on the internal walls of the

spray tower was less, often about 20 to 50% less, than when the polyacrylate was not present in the formula. The tower throughput was increased and it appeared that the fines content of the product was diminished. The diminution of buildup and of fines production resulted in a significantly lower proportion of recycling being required.

Example 3C

Detergent products were made from spray dried beads by spraying onto the tumbling bead surfaces thereof a normally waxy nonionic detergent, either Neodol 23—6.5 or Neodol 23—7, in heated liquid state, in such quantity as to result in a final product containing 20.7% of nonionic detergent, and proteolytic enzyme (Alcalase) was applied in powdered form to result in a 1.32% concentration in the product. Perfume was sprayed onto the product to produce a 0.25% concentration therein. The resulting detergent products were of bulk density of about 0.7 gr/ml and contained 27.0% of zeolite (hydrate), 20.7% of the nonionic detergent, 18.17% of sodium carbonate (some of which was produced by decomposition of sodium bicarbonate), 12.9% of sodium bicarbonate, 10.6% of sodium silicate, 4.39% of moisture, 1.32% of enzyme, 1.71% of fluorescent brightener, 1.51% of magnesium sulphate, 0.25% of citric acid (in citrate form), 0.25% of perfume, 0.2% of ultramarine blue and 1.0% of sodium polyacrylate. The detergent made, of such formula, was an excellent heavy duty laundry detergent and was especially useful for washing household laundry in automatic washing machines. It was physically and aesthetically advantageous and attractive because it was non-dusting and extremely freely flowing, allowing it to be packaged in narrow-necked glass and plastic bottles from which it may flow readily for dispensing. In comparative tests against similar compositions not containing the polyacrylate, the compositions of this invention are found to exhibit improved soil removal and stain removal activities when tested on various test soils and stains on a wide variety of test fabrics, including cotton, polyester-cotton mixtures, polyesters and other synthetics. With respect to stain removal, it has often been found that the polyacrylates are often more effective against stains than larger quantities of more expensive enzymes, which are usually more specific in stain removal action and therefore are not as effective against combinations of stains found in many wash loads. Compositions of the invention containing the polyacrylate also exhibit excellent anti-redeposition effects, helping to prevent dirtying of the laundry by redeposition of removed soil.

The manufacturing procedures may be like those described in Example 1 and different processing aids and adjuvants may be employed, as set forth in that example. Also, certain adjuvants may be omitted, as mentioned in Example 1. The crutcher mix temperature may be modified as by elevation to 52°C, and the

proportions of the various components may be varied $\pm 10\%$, $\pm 20\%$ and $\pm 30\%$, while still maintaining them within the ranges previously given, and workable crutcher mixes that result in the desired beads and detergent compositions will be obtainable. Various compounds may be added as aqueous solutions, providing that the amounts of moisture added with them are subtracted from the crutcher formula amount. Other orders of addition may be employed. Instead of Zeolite 4A, Zeolites X and Y may be substituted, as may be other types of Zeolite A. While it is preferred to employ the hydrated Zeolite 4A of this example, various degrees of hydration of the zeolite are acceptable and in some instances nearly anhydrous crystalline zeolites or amorphous zeolites may be employed. Varying the amount of polyacrylate within the range given, to 1.0 and 1.7% in the base beads, for example, still results in useful products but those containing larger proportions of the sodium polyacrylate will usually be more effective in cleaning, absorbing nonionic detergent and promoting of improved tower processings. It will usually not be desirable to utilize more than about 2% of the polyacrylate because its effectiveness decreases at higher concentrations and the gains obtained are not economically desirable.

Examples 4A to 4C

Example 4A1

A crutcher mix like that of Example 3A was made but utilizing Alcosperse 107, a sodium polyacrylate solution wherein the polyacrylate is of a molecular weight of about 1,000 or 1,000 to 2,000, and which is a clear amber liquid of 30% solids content. The proportion of Alcosperse 107 employed was equivalent in solids content to the Alcosperse 107D utilized in Example 1. No other significant changes were made in the formula, compared to Example 3, nor in the processing method.

Examples 4A2 and 4A3

Instead of Alcosperse 107, proportionate amounts of a solids basis of Alcosperses 104 (25% solids) or 149 (40% solids content) were substituted but the results with the 107 type product are better and therefore the Alcosperse 107 is preferred.

Example 4B

Base beads were made by spray drying the crutcher mix of Example 4A1 by the method of Example 3B.

Example 4C

The base beads of Example 4B were converted by the method described in Example 3C to finished product, employing Neodol 23—6.5 as the nonionic detergent. The product made when Alcosperse 107 was utilized was an excellent non-phosphate detergent, useful as a heavy duty built laundry detergent, which was effective against a wide variety of stains, including liquid

cosmetic make-up and synthetic sebum (Spangler type). A ten-member test panel also significantly preferred such a product to a comparable one from which the Alcosperse 107 had been omitted. Similarly, such preference was indicated by instrumental measurements of washed materials. The test were performed on cotton, Dacron-cotton and nylon fabrics, and test conditions include machine washing in 150 ppm hardness water with a detergent composition concentration of 0.07% by weight and with the water temperature at 49°C.

The same processing advantages mentioned in Example 3 were observable, including excellent dispersion of materials in the crutcher and clean spraying of the product. The base beads were of measurably greater porosity than controls (minus polyacrylate). Yet, bulk density was not lowered more than a few percent, e.g., 3% which is important for such concentrated products. Similar results were obtainable by varying the formula contents of the various other essential components ± 15 and $\pm 30\%$, keeping the proportions within the ranges specified. Also, such results were obtainable when other Zeolite A's were utilized, of different degrees of hydration, e.g., 15 and 22%, and when the polyacrylates within the molecular weight range of 1,000 to 5,000 were employed. Preferably such polyacrylates are sodium neutralized, either completely or to at least about 50%, but less neutralized ones can be used.

Results similar to those reported herein are also obtainable when fluorescent brightener, perfume, enzyme and processing aids (citric acid and magnesium sulphate) are eliminated but in such cases care should be taken that spray drying is effected soon after manufacture of the crutcher mix so that such mix does not set in the crutcher. Also, as is evident, the individual contributions of the omitted materials will be lost, but the product will still be a good laundry detergent, as described, the crutcher mix will be well dispersed and will be dried easily, and the base beads will be of improved porosity.

Examples 5A to 5C

Example 5A

A 4536 kg batch of crutcher mix for spray drying base beads of this invention which do not contain water soluble silicate was made by adding to a crutcher 2,132 kg of deionized water at a temperature of about 27°C, and sequentially, and initially with low speed crutcher mixing, admixing with it 47.2 kg of Tinopal 5BM Extra Conc. (CIBA—Geigy); 5.9 kg of ultramarine blue powder, 3.2 kg of sodium polyacrylate (Alcosperse 107D), 957.5 kg of Linde hydrated zeolite 4A (20% water of crystallization), 283.5 kg of Thixo-Jel No. 1 (bentonite) 714.4 kg of sodium bicarbonate (industrial grade), 351.1 kg of sodium carbonate (natural soda ash) and 41.3 kg of titanium dioxide (Anatase). During mixing of the various components the mixer speed was increased to

medium and ultimately to high and after addition of all the constituents, which took approximately fifteen minutes, mixing was continued for about an hour (in some cases as long as four hours of mixing may occur), during which time some of the water present, e.g., about 90.7 to 272.2 kg may be lost by evaporation, and may be replenished, if desired. During the mixing time the crutcher slurry was continuously mobile and did not gel, set or cake. Because bicarbonate partially decomposes to carbonate during spray drying, the amounts of bicarbonate and carbonate in the crutcher formulation may be varied, depending on the spray tower operating characteristics.

15 Example 5B

Starting about five minutes after all the components of the crutcher mix are present, the mix of Example 5A was dropped from the crutcher to a pump, which pumped it at a pressure which was at about 21 kg/sq cm into the top of a countercurrent spray tower wherein the initial temperature was about 430°C and the final temperature was about 105°C. The essentially inorganic base beads resulting were of a bulk density of about 0.6 to 0.7 gr/ml, a percentage initial adhesion less than 10%, of a particle size range substantially between 10 and 60 mesh, U.S. Sieve Series (they are screened to such range), and of a fines characteristic (through U.S. Sieve No. 50) of about 15%. The moisture content of the beads was in the range of 1 to 10%. The base beads were found to be free-flowing (80% flow index), non-tacky, satisfactorily porous, yet firm on the surfaces thereof, and were capable of readily absorbing significant proportions of liquid nonionic detergent without becoming objectionably tacky.

Example 5C

Detergent products were made from the spray dried beads by spraying onto the tumbling bead surfaces thereof a normally waxy nonionic detergent. Neodol 23—6.5 was used but Neodol 23—7 or Neodol 25—7 may be substituted. The nonionic detergent was in heated liquid state (at a temperature of about 45°C). The quantity sprayed was such as to result in a final product containing about 20% of nonionic detergent. Proteolytic enzyme (Alcalase) was applied in powdered form to result in about a 1.5% concentration in the product, and perfume was sprayed onto the product to produce a 0.25% concentration therein. The resulting detergent compositions were of a bulk density of about 0.7 to 0.8 gr/ml, and contained 32.45% of zeolite (hydrated), 19.7% of the nonionic detergent, 18.5% of sodium carbonate (some of which was produced by decomposition of sodium bicarbonate), 13.5% of sodium bicarbonate, 1.3% of free water, 1.4% of enzyme, 1.6% of fluorescent brightener, 0.25% of perfume, 0.2% of ultra-marine blue, 9.6% of bentonite (Thixo-Jel) 0.1% of sodium polyacrylate and 1.4% of titanium dioxide. The detergent made, of the above formula, was an excellent

heavy duty laundry detergent, useful for washing household laundry in automatic washing machines. It was non-dusting and extremely free flowing. Detergent compositions like that of this example containing bentonite, as described, were found to be of significantly improved calcium ion binding rates but more importantly, they leave less zeolite residue on laundry washed with them in an automatic washing machine, especially when such laundry is line dried, than do similar compositions containing less bentonite and with sodium silicate in the spray dried base beads. This difference is accentuated when the wash-water is high in hardness, e.g., 200 ppm, as calcium carbonate, the wash water is cold, and a gentle agitation cycle is employed.

Manufacturing procedures, with variations, such as are described in Example 1, may be followed and certain adjuvants may be omitted, as therein mentioned. Proportions of the various components may be varied $\pm 10\%$, $\pm 20\%$ and $\pm 30\%$, while still maintaining them within the ranges previously given, and workable crutcher mixes that result in the desired beads and detergent compositions will be obtainable. The crutcher mix solids contents may be varied over the range recited, e.g., to 45% and 65%, and good mixing and spray drying are obtainable. Instead of using Zeolite 4A, Zeolites X and Y may be substituted as may be other types of Zeolite A. While it is preferred to employ the hydrated Zeolite 4A of this example, various degrees of hydration of the zeolite are acceptable and in some instances nearly anhydrous crystalline zeolites or amorphous zeolites may be employed. Varying the amount of bentonite within the range given, to 10 to 17%, for example, still results in useful products but those containing the larger proportions of bentonite will usually be more effective in helping to prevent zeolite deposition on laundry.

105 Example 5D

The improvement noted in the low soluble silicate or non-silicate detergent compositions of this invention depositing less residue on washed laundry was verified by testing the described product against a control product of essentially the same formula, with no bentonite present and containing about 8% of sodium silicate. In such evaluation a Whirlpool Suds Save model washing machine was employed, with the washing periods being eight minutes at a gentle wash cycle. The detergent composition concentration was 0.06%, the wash water was of mixed calcium and magnesium hardness with a total of 200 ppm hardness, as calcium carbonate, and the water temperature was 24°C. The items washed were 100% cotton; 100% polyester; 85% acetate and 15% nylon; and 65% polyester; and 25% cotton. The wash was observed wet and after line drying. No residue was observed in any such case with product of Example 5C. When the control formula detergent composition of Example 5D was tested,

moderate residue was observed on all test specimens.

The results of the practical residue test described above are verified by weighing residue deposited on a denim test material. In such test, the detergent composition to be tested is filtered through a sample of denim material, with a detergent being in solution-suspension of 0.12% concentration in 200 ppm (as CaCO_3) hardness water at 24°C. The weight of residue on the cloth is noted, and compared to that in a control test. By such testing between Examples 5C and 5D the percentage of residue of Example 5C, compared to the control (Example 5D) was about 75%, which is considered to be a significant improvement.

The percentage initial adhesion previously referred to, which is a measure of tackiness of detergent products, is tested as follows: 10 grams of base beads (or detergent composition, in some cases) are placed evenly between two watch glasses, both of which are about 23 cm in diameter, with a weight of 500 grams on top of the upper watch glass (both watch glasses being concave side up). After standing about five minutes, the weight and top watch glass are removed and the bottom watch glass is inverted, after which the product remaining stuck to such watch glass is weighed. The percentage initial adhesion is the number of grams of product remaining on such watch glass divided by 10 and multiplied by 100.

The flow index of the product is determined by the following flow test. In this flow test the volumetric flow rates of base beads (and in some cases final product) and standardized Ottawa sand (-20 +60, U.S. Sieve Series sieve) are compared by measuring the times required for complete emptying of a 1.9 litre Mason jar through a 2.2 cm diameter hole in a nozzle attached to the cap thereof. The flow index is the time for the sand flow divided by the time for the test product flow, expressed as a percentage.

Examples 6A to 6C

Examples 5A to 5C were repeated, on a reduced scale, without the polyacrylate being present in the reduced crutcher mix. The throughput rate through the spray tower was appreciably diminished and the capability of the base beads for absorbing nonionic detergent was also less (or the product made somewhat tackier if the same proportion of nonionic detergent was applied). However, the crutcher mix did not freeze in the crutcher, the base beads could be manufactured by spray drying and the resulting detergent composition, although lower in nonionic detergent content, e.g., 17% nonionic detergent, to maintain flowability and non-tacky properties, was still a useful product and of satisfactory flow characteristics.

Examples 7A to 7C

Examples 5A to 5C were repeated, with 2% of sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:2.4 being

added to the crutcher as a 47.5% solids aqueous solution. The product made did not gel in the crutcher, in normal manufacturing procedures, but it was desirable to utilize magnesium sulphate and citric acid as processing aids to prevent gelation or freezing when the holdup time was greater than normal. Also, the detergent composition made leaves more residue on washed laundry, which is more noticeable when the colours of such laundry are dark.

Examples 8A to 8C

Examples 5A to 5C were repeated with 5% of hydrous sodium silicate powder (Britesil) being post-added with the enzyme powder. Such post-added silicate did not appear to adversely affect zeolite deposition on washed laundry significantly and did aid in corrosion prevention with respect to aluminium washing machine parts, and in water softening and detergent building.

Examples 9A to 9C

Examples 5A to 5C were repeated with only water, zeolite, bentonite, sodium carbonate, sodium bicarbonate and sodium polyacrylate being present in the crutcher mix and in the base beads and with only nonionic detergent being post-added thereto. The product resulting was of satisfactory deterative properties but was not commercially acceptable for aesthetic reasons because of the lack of perfume therein. Also, it did not clean us well, due to the absence of enzyme and did not have the bluing and brightening effects that the ultramarine blue and fluorescent material contribute to the other formulations.

Claims

1. A crutcher slurry which comprises by weight from 40 to 70% of solids and 60 to 30% of water, which solids content, on a 100% solids basis, comprises A) about 10 to 25% sodium carbonate, B) 15 to 30% sodium bicarbonate, C) 20 to 40% of water softening aluminium silicate, D) 0 to 18% sodium silicate, E) 1 to 20% bentonite and F) 0.05 to 2% polyacrylate of molecular weight in the range of 1,000 to 5,000, or A), B), C), D and E) or A), B), C), D) and F).

2. A crutcher slurry as claimed in claim 1 in which the weight ratio of sodium bicarbonate:sodium carbonate is within the range of 0.5:1 to 2:1.

3. A crutcher slurry as claimed in claim 1 or claim 2 which comprises, on an anhydrous basis, 1.5 to 2.5% of magnesium sulphate, 0.2 to 0.5% of sodium citrate, 0.2 to 0.4% of ultramarine blue, 1.5 to 3% of fluorescent brightening agent.

4. A crutcher slurry as claimed in claims 1, 2 or 3 which comprises 0.1 to 2% of the said polyacrylate.

5. A crutcher slurry as claimed in claim 4 which comprises 0.5 to 1.5% of the said polyacrylate.

6. A crutcher slurry as claimed in anyone of the preceding claims in which the polyacrylate is a sodium polyacrylate of molecular weight in the range of 1,000 to 3,000.

7. A crutcher slurry as claimed in claim 1, substantially as specifically described herein with reference to anyone of Examples 1A, 2A, 3A, 4A, 5A, 6A, 7A, 8A or 9A.

5 8. Base beads whenever made by spray drying a crutcher slurry as claimed in anyone of claims 1 to 7.

9. Free flowing, spray dried base beads, comprising A) by weight from about 15 to 30% of sodium carbonate, B) about 10 to 22% of sodium bicarbonate, C) about 10 to 50% of water softening aluminium silicate, D) about 0 to 18% of sodium silicate, E) about 1 to 20% of bentonite and F) about 0.05 to 2% of polyacrylate of molecular weight in the range of 1,000 to 5,000, or comprising A, B, C, D, and E or A, B, C, D, and F.

10. Free flowing, spray dried base beads, useful, by application of detergent thereto, for manufacture of particulate built synthetic organic detergent products, which, due to the presence of the bentonite therein, leave lesser amounts of deposits, after rinsing, on fabrics washed with such product, compared to fabrics washed with such products from which the bentonite is omitted, comprising by weight from about 15 to 30% of sodium carbonate, about 10 to 22% of sodium bicarbonate, about 10 to 50% of water softening aluminium silicate, about 0 to 18% of sodium silicate and about 1 to 20% of bentonite and/or about 0.05 to 2% of polyacrylate of molecular weight in the range of 1,000 to 5,000.

11. Beads as claimed in claim 10 in which the polyacrylate is present in an amount of 0.1 to 2%.

35 12. Beads as claimed in claim 10 or claim 11 having a bulk density of 0.6 to 0.9 gr/cc and particle sizes in the range of No. 10 to 100, U.S. Sieve Series.

40 13. Beads as claimed in claim 12 having a bulk density of 0.6 to 0.8 gr/cc.

45 14. Beads as claimed in anyone of claims 9 to 13 wherein the aluminosilicate is a hydrated water softening sodium zeolite containing from 15 to 25% by weight thereof of water of hydration and having an exchange capacity for calcium ions which is in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite.

50 15. Beads as claimed in anyone of claims 9 to 14 in which the zeolite has an ultimate mean particle size in the range 3 to 12 microns.

55 16. Beads as claimed in anyone of claims 9 to 15 in which the zeolite has a calcium ion exchange capacity of 250 to 350 mg. eq/g of calcium carbonate hardness per gram of anhydrous zeolite.

60 17. Beads as claimed in anyone of claims 9 to 16 in which the zeolite has a hardness depletion rate residual hardness less than 0.01 mg/l per litre in ten minutes.

18. Beads as claimed in anyone of claims 9 to 17 in which the zeolite is Zeolite A.

65 19. Beads as claimed in anyone of claims 9 to 18, which contain bentonite, the bentonite being a swelling clay.

20. Beads as claimed in claim 19 in which the bentonite is a swelling clay having a swelling capacity, in water, of 3 to 15 ml/gr.

70 21. Beads as claimed in claim 20 in which the bentonite has a swelling capacity in the range 7 to 15 ml/gr.

22. Beads as claimed in claim 19, 20 or 21 in which the bentonite exhibits a viscosity of 3 to 30 centipoises at 6% concentration in water.

75 23. Beads as claimed in claim 22 in which the bentonite exhibits a viscosity of 8 to 30 centipoises at 6% concentration of water.

80 24. Beads as claimed in anyone of claims 19 to 23 in which the bentonite is beneficiated Wyoming bentonite.

25. Beads as claimed in anyone of claims 9 to 24 comprising 0.05 to 0.5% of polyacrylate of molecular weight in the range of 1,000 to 5,000.

85 26. Beads as claimed in anyone of claims 9 to 25 in which the polyacrylate has a molecular weight in the range 1,000 to 3,000.

27. Beads as claimed in anyone of claims 9 to 25 in which the polyacrylate is sodium polyacrylate.

90 28. Beads as claimed in anyone of claims 9 to 25 containing sodium silicate which has an $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range 1:1.4 to 1:3.

29. Beads as claimed in claim 28 in which the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio is in the range 1:2 to 1:2.4.

95 30. Beads as claimed in anyone of claims 9 to 28 containing sodium silicate in an amount of 4 to 18%.

31. Beads as claimed in claim 30 in which the amount of sodium silicate is 4 to 12%.

100 32. Beads as claimed in anyone of claims 9 to 31 in which the weight ratio of sodium carbonate:sodium bicarbonate is within the range of about 1:1 to 3:1.

105 33. Beads as claimed in claim 32 in which the weight ratio of sodium carbonate:sodium bicarbonate is within the range of 1:1 to 2:1.

110 34. Beads as claimed in anyone of claims 9 to 33 comprising by weight from 15 to 30% of sodium carbonate, 10 to 22% of sodium bicarbonate, 10 to 50% of water softening aluminium silicate, 0 to 18% of sodium silicate and 1 to 20% of bentonite and/or 0.05 to 2% of polyacrylate of molecular weight in the range of 1,000 to 5,000.

115 35. Beads as claimed in anyone of claims 9 to 34 comprising from 20 to 25% of sodium carbonate, 13 to 19% of sodium bicarbonate, 30 to 37% of hydrated zeolite, 7 to 15% of sodium silicate, 0.5 to 1.5% of sodium polyacrylate and 3 to 10% of water, exclusive of the water of hydration of the zeolite.

120 36. Beads as claimed in anyone of claims 9 to 35 comprising 0 to 3% of sodium silicate and 1 to 20% of bentonite.

125 37. Beads as claimed in anyone of claims 9 to 36 comprising from 20 to 30% of sodium carbonate, 13 to 22% of sodium bicarbonate, 35 to 45% of hydrated zeolite, 0% of sodium silicate, 5 to 20% of bentonite and 1 to 15% of water, exclusive of the water of hydration of the zeolite.

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38. Beads as claimed in anyone of claims 9 to 35 comprising 20 to 40% of water softening aluminium silicate, 4 to 12% of sodium silicate and 1 to 15% of bentonite.

39. Beads as claimed in anyone of claims 9 to 35 comprising from 20 to 25% of sodium carbonate, 13 to 19% of sodium bicarbonate, 30 to 37% of hydrated zeolite, 5 to 8% of sodium silicate, 5 to 8% of bentonite and 4 to 10% of water, exclusive of the water of hydration of the zeolite.

40. Beads as claimed in claim 36 of a bulk density of 0.6 to 0.9 gr/cc and particle sizes in the range of No. 10 to 100, U.S. Sieve Series, wherein the aluminosilicate is a hydrated water softening sodium zeolite containing from 15 to 25% by weight thereof of water of hydration and has an exchange capacity for calcium ions which is in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite, the sodium silicate is of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:1.4 to 1:3 and the weight ratio of sodium carbonate:sodium bicarbonate is within the range of about 1:1 to 3:1.

41. Beads as claimed in claim 40 comprising from 20 to 30% of sodium carbonate, 13 to 22% of sodium bicarbonate, 35 to 45% of hydrated zeolite, 0% of sodium silicate, 5 to 20% of bentonite and 1 to 15% of water, exclusive of the water of hydration of the zeolite, and in which the zeolite is Zeolite A, of ultimate mean particle sizes in the range of 3 to 12 microns, of a calcium ion exchange capacity of 250 to 350 mg. eq/g and of a hardness depletion rate residual hardness less than 0.01 mg/l per litre in ten minutes, the bentonite is a swelling clay having a swelling capacity, in water, of 3 to 15 ml/g and a viscosity of 3 to 30 centipoises at 6% concentration of water, and the weight ratio of sodium carbonate:sodium bicarbonate is within the range of 1:1 to 2:1.

42. Beads as claimed in claim 41 which are of a bulk density of 0.6 to 0.8 gr/cc, comprising 0.05 to 0.5% of sodium polyacrylate of molecular weight in the range of 1,000 to 5,000 and wherein the bentonite is beneficiated Wyoming bentonite of swelling capacity in the range of 7 to 15 ml/gr and of viscosity in the range of 8 to 30 centipoises at 6% concentration in water.

43. Beads as claimed in claim 38 of a bulk density of 0.6 to 0.9 g/cc and particle sizes in the range of No. 10 to 100, U.S. Sieve Series, wherein the aluminosilicate is a hydrated water softening sodium zeolite containing from 15 to 25% by weight thereof of water of hydration and has an exchange capacity for calcium ions which is in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite, the sodium silicate is of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:1.4 to 1:3 and the weight ratio of sodium carbonate:sodium bicarbonate is within the range of about 1:1 to 3:1.

44. Beads as claimed in claim 35 comprising

from 20 to 25% of sodium carbonate, 13 to 19% of sodium bicarbonate, 30 to 37% of hydrated zeolite, 5 to 8% of sodium silicate, 5 to 8% of bentonite and 4 to 10% of water, exclusive of the water of hydration of the zeolite, and in which the zeolite is Zeolite A, of ultimate mean particle sizes in the range of 3 to 12 microns, of a calcium ion exchange capacity of 250 to 350 mg eq/g and of a hardness depletion rate residual hardness less than 0.01 mg/l in ten minutes, the sodium silicate is of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:2 to 1:2.4, the bentonite is a swelling clay having a swelling capacity in water of 3 to 15 ml/gram and a viscosity of 3 to 30 centipoises at 6% concentration in water, and the weight ratio of sodium carbonate-sodium bicarbonate is within the range of 1:1 to 2:1.

45. Beads as claimed in claim 44 which are of a bulk density of 0.6 to 0.8 gr/cc, comprising from 0.1 to 2% of sodium polyacrylate of molecular weight in the range of 1,000 to 5,000, and wherein the bentonite is beneficiated Wyoming bentonite of swelling capacity in the range of 7 to 15 ml/g and of viscosity in the range of 8 to 30 cp. at 6% concentration in water.

46. Beads as claimed in claim 35 comprising 20 to 40% of water softening aluminium silicate, 4 to 18% of sodium silicate and 0.1 to 2% of polyacrylate of molecular weight in the range of 1,000 to 5,000.

47. Beads as claimed in claim 46 of a bulk density of 0.5 to 0.8 gr/cc and particle sizes in the range of No. 10 to 100, U.S. Sieve Series, wherein the aluminium silicate is a hydrated water softening sodium zeolite containing from 15 to 25% by weight thereof of water of hydration and has an exchange capacity for calcium ions which is in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite, the sodium silicate is of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:1.4 to 1:3 and the weight ratio of sodium carbonate:sodium bicarbonate is within the range of about 1:1 to 3:1.

48. Beads as claimed in claim 47 comprising from 20 to 25% of sodium carbonate, 13 to 19% of sodium bicarbonate, 30 to 37% of hydrated zeolite, 7 to 15% of sodium silicate, 0.5 to 1.5% of sodium polyacrylate and 3 to 10% of water, exclusive of the water of hydration of the zeolite, and in which the zeolite is Zeolite A, of ultimate mean particle sizes in the range of 3 to 12 microns, of a calcium ion exchange capacity of 250 to 350 mg. eq/g and of a hardness depletion rate residual hardness less than 0.01 mg/l in ten minutes, the sodium silicate is of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:2 to 1:2.4, the polyacrylate is sodium polyacrylate of molecular weight in the range of 1,000 to 3,000 and the weight ratio of sodium carbonate:sodium bicarbonate is within the range of 1:1 to 2:1.

49. Beads as claimed in claim 9 substantially as specifically described herein with reference to anyone of Examples 1B, 2B, 3B, 4B, 5B, 6B, 7B, 8B or 9B.

50. A method of manufacturing base beads as claimed in anyone of claims 9 to 49 which comprises spray drying a crutcher mix containing 40 to 75% of solids, the said solids having a composition corresponding to that recited in the said claims, in an aqueous medium, or a crutcher mix as claimed in anyone of claims 1 to 8 and during such spray drying decomposing a portion of the sodium bicarbonate present therein to sodium carbonate.

51. A method as claimed in claim 50 which comprises spray drying a crutcher mix containing 50 to 65% of solids, the said solids having a composition corresponding to that recited in claim 42 in an aqueous medium, and during such spray drying decomposing a portion of the sodium bicarbonate present therein to sodium carbonate and thereby increasing the capacity of the resulting beads for absorbing nonionic detergent in liquid state due to the release of carbon dioxide and the presence of the polyacrylate.

52. A method as claimed in claim 50 which comprises spray drying a crutcher mix containing 50 to 65% of solids, the said solids having a composition corresponding to that recited in claim 45 in an aqueous medium, and during such spray drying decomposing a portion of the sodium bicarbonate present therein to sodium carbonate and increasing the capacity of the resulting beads for absorbing nonionic detergent in liquid state due to the presence of the polyacrylate.

53. A method as claimed in claim 50 which comprises making a crutcher slurry of improved gelation and setting retarding characteristics comprising by weight from 40 to 70% of solids and 60 to 30% of water, of which solids content, on a 100% solids basis, about 10 to 25% is sodium carbonate, 15 to 30% is sodium bicarbonate, with the weight ratio of sodium carbonate:sodium bicarbonate being within the range of 0.5:1 to 2:1, 20 to 40% is water softening aluminosilicate, 5 to 18% is sodium silicate and 0.1 to 2% of polyacrylate of molecular weight in the range of 1,000 to 5,000, and spray drying such crutcher mix in a spray drying tower.

54. A method of manufacturing base beads as claimed in claim 50 substantially as specifically described herein with reference to anyone of Examples 1B, 2B, 3B, 4B, 5B, 6B, 7B, 8B or 9B.

55. Beads as claimed in claim 9 whenever made by a method as claimed in anyone of claims 50 to 54.

56. A detergent composition which comprises beads as claimed in anyone of claims 9 to 49 or claim 55 having absorbed in them a nonionic detergent so that the percentage of such nonionic detergent in the composition is within the range of 8 to 30%.

57. A detergent composition as claimed in claim 56 in which the nonionic detergent is a condensation product of 6 to 12 mols of ethylene

oxide and a higher fatty alcohol of 12 to 16 carbon atoms.

58. A detergent composition as claimed in claim 56 or claim 57 in which the proportion of nonionic detergent in the composition is within the range of 15 to 22%.

59. A detergent composition as claimed in claim 56, 57 or 58 which also comprises 0.5 to 3% of an enzyme.

60. A detergent composition as claimed in anyone of claims 56 to 59 which comprises beads as claimed in claim 41 having absorbed in them a nonionic detergent so that the percentage of such nonionic detergent in the detergent composition is within the range of 8 to 25%.

61. A detergent composition as claimed in anyone of claims 56 to 59 which comprises beads as claimed in claim 42 having absorbed in them a nonionic detergent so that the percentage of such nonionic detergent in the composition is within the range of 8 to 25%.

62. A detergent composition as claimed in anyone of claims 56 to 59 which comprises beads as claimed in claim 44 having absorbed in them a nonionic detergent so that the percentage of such nonionic detergent in the detergent composition is within the range of 8 to 25%.

63. A detergent composition as claimed in anyone of claims 56 to 59 comprising by weight from 13 to 28% of sodium carbonate, 8 to 18% of sodium bicarbonate, 15 to 35% of water softening aluminium silicate, 3 to 14% of sodium silicate, 0.1 to 1.6% of polyacrylate of a molecular weight in the range of 1,000 to 5,000 and 8 to 30% of a nonionic detergent.

64. A detergent composition as claimed in claim 63 of a bulk density of 0.6 to 0.9 gr/cc and particle sizes in the range of No 10 to 100, U.S. Sieve Series, wherein the aluminium silicate is hydrated Zeolite A containing from 15 to 25% by weight thereof of water of hydration, the sodium silicate is $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:1.4 to 1:3, the polyacrylate is sodium polyacrylate of molecular weight in the range of 1,000 to 3,000, the weight ratio of sodium carbonate:sodium bicarbonate is within the range of 1:1 to 2:1, the nonionic detergent is a condensation product of 5 to 12 moles of ethylene oxide and a mole of higher fatty alcohol of 12 to 16 carbon atoms and which composition contains water, exclusive of the water of hydration of the zeolite, and in which composition the percentages of components are within the ranges of 16 to 21% of sodium carbonate, 10 to 15% of sodium bicarbonate, 22 to 32% of hydrated zeolite, 8 to 13% of sodium silicate, 0.5 to 1.5% of sodium polyacrylate, 3 to 6% of moisture and 10 to 22% of nonionic detergent.

65. A detergent composition as claimed in claim 56 substantially as specifically described herein with reference to anyone of Examples 1C, 2C, 3C, 4C, 5C, 6C, 7C, 8C or 9C.